UTILIZATION OF WASTE

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CERAMIC TILES MADE OF GRANULAR TECHNOGENIC RAW MATERIALS

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Sintering and properties of granular compositions containing quartz-feldspar sand (ore processing waste) are studied. Low-melting binders having mineralogical compatibility with the sand grains, reaction activity toward their surface, and a favorable phase composition (regarding sintering and ceramic properties) are developed. The effect of the mixture composition, binder content, grain composition of the sand, and firing temperature on the sintering of mixtures intended for production of tiles for various purposes is established. The tiles thus obtained successfully imitate the surface of granite-like natural stones.

The possibility of ceramic tile production from granular technogenic raw materials without their preliminary grinding to a fine state substantially reduces the cost of the tile.

We performed a study of the sintering and properties of granular compositions. A theoretical approach to their formation was substantiated earlier by P. P. Budnikov, P. I. Bozhenov, and A. P. Merkin [1 – 3].

Quartz-feldspar enrichment "tails" (Molibden JSC (Khakassiya)) having a dense glassy grain structure and small losses (2.5%) upon calcination are considered. The sand contains quartz (25 – 38%) and feldspar (51 – 56%) in the form of orthoclase, albite, and anorthite [4]. The sand grain size ranges within 0.10 – 0.63 mm (Table 1).

Unlike the coarse-grained sand, which contains 16.8% grains more than 0.63 mm in diameter, the fine-grained sand contains only 4.1% large-size grains. The coarse-grained sand is almost free of grains smaller than 0.16 mm, whereas the fine-grained sand contains them in an amount of 16.1%. The sand sampling was performed using a selective method adopted at the silicate factory.

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TABLE 1

Sample	Riddling, %, on mesh No.			
	063	0315	016	< 016
1	16.8	38.1	44.9	0.2
2	7.3	23.4	60.9	8.4
3	4.1	18.2	61.6	16.1

To ensure sintering of granular compositions we first developed compositions of ceramic binders on the basis of two-component mixtures of clays and cullet. Binders to be developed should be low-melting and should readily interact with the sand grain surface, possess mineralogical compatibility with the grains, and exhibit rather high plasticity to ensure the required compressibility and strength of the compact.

Local plastic clays (19 – 29) were used as raw materials: low-melting kaolinite-montmorillonite Beloyarskoe (B) clay and refractory kaolinite-montmorillonite Izykhskoe (Iz) clay [4] ground to a size that ensures complete passage through mesh No. 014, and cullet (4 – 5% riddling on mesh No. 005).

It was found to be advantageous to use binders based on Beloyarskoe clay containing 20 – 35% cullet or Isykhskoe clay containing 20 – 50% of cullet, respectively.

Analysis of the binder melt crystallization was performed for two phase diagrams ($CaO – Al_2O_3 – SiO_2$ and $Na_2O – Al_2O_3 – SiO_2$) because of almost the same amount of calcium and sodium oxides in the binders (Table 2). The analysis revealed the possibility of formation of phases (upon firing) capable of ceramic sintering and improving the properties of the ceramics.

According to the phase diagram of $Na_2O – Al_2O_3 – SiO_2$, albite (76.7 – 95.3%) containing nepheline (6.3 – 13.2%) or sodium bisilicate (6.7 – 23.3%) additives, which promote sintering of the binders (Table 3 and 4), is a preferred phase prior to the onset of crystallization of triple eutectics. According to the phase diagram of $CaO – Al_2O_3 – SiO_2$, quartz (39.1 – 55.4%) and anorthite (44.6 – 60.8%) additives enhance the affinity of the binders to sand grains composed of

TABLE 2

Cullet weight content in the binder, %	Weight content, %							
	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O
Izykhskoe clay based binder:								
20	67.95	15.76	0.27	4.57	5.82	1.93	2.93	0.79
30	67.79	14.72	0.24	4.22	5.91	2.10	4.16	0.85
40	67.75	13.38	0.20	3.87	6.09	2.29	5.39	1.02
50	67.68	12.09	0.17	3.52	6.29	2.47	6.61	1.18
Beloyarskoe clay based binder:								
20	65.68	12.08	0.16	7.43	6.81	4.26	2.94	0.73
30	65.81	11.30	0.14	6.33	6.77	4.14	4.16	0.80
40	66.14	10.71	0.12	6.41	6.83	4.13	5.40	0.25
50	66.27	9.73	0.10	5.31	6.90	3.93	6.61	1.15

TABLE 3

Cullet weight content in the binder, %	Area of figurative (symbolic) points of binder melts on the phase diagram		Melting point (°C) according to phase diagram	
	$Na_2O – Al_2O_3 – SiO_2$	$CaO – Al_2O_3 – SiO_2$	$Na_2O – Al_2O_3 – SiO_2$	$CaO – Al_2O_3 – SiO_2$
Izykhskoe clay based binder:				
20	Albite – mullite – quartz	Anorthite – mullite – quartz	1050	1345
30	Sodium bicilicate – albite – quartz	Wollastonite – anorthite – quartz	740	1165
40	The same	The same	740	1165
50	″	″	740	1165
Beloyarskoe clay based binder:				
20	Sodium bisilicate – albite – nepheline	″	732	1165
30	The same	″	732	1165
40	″	″	732	1165
50	″	″	732	1165

TABLE 4

Cullet weight content in the binder, %	Weight content of phases (%) prior to the onset of crystallization of triple eutectics according to the phase diagram					
	$Na_2O – Al_2O_3 – SiO_2$				$CaO – Al_2O_3 – SiO_2$	
	sodium bisilicate	albite	nepheline	mullite	quartz	anorthite
Izykhskoe clay based binder:						
20	–	95.3	–	4.7	39.1	60.8
30	6.7	93.3	–	–	50.0	50.0
40	13.4	86.6	–	–	52.7	47.3
50	23.3	76.7	–	–	55.4	44.6
Beloyarskoe clay based binder:						
20	–	86.8	13.2	–	41.9	58.1
30	–	89.7	10.2	–	43.2	56.8
40	–	93.7	6.3	–	44.6	55.4
50	20.0	80.0	–	–	59.5	40.5

the same phases, and anorthite is capable of improving the physicotechnical properties of the binders as well.

Experimental data on binder sintering and x-ray phase analysis of fired samples match the calculation. Binders developed on the basis of Beloyarskoe and Izykhskoe clays (which contain 20 – 35% and 20 – 50% cullet, respectively) exhibit good sintering at temperatures of 950 – 1100°C and possess a certain interval of the sintered state: 20 – 30°C and 40 – 50°C, respectively, for Beloyarskaya and Izykhskoe clays at the maximum cullet content in their composition (see Figs. 1 and 2). Reflections of albite, nepheline, quartz, and anorthite are clearly seen on the x-ray pictures of the

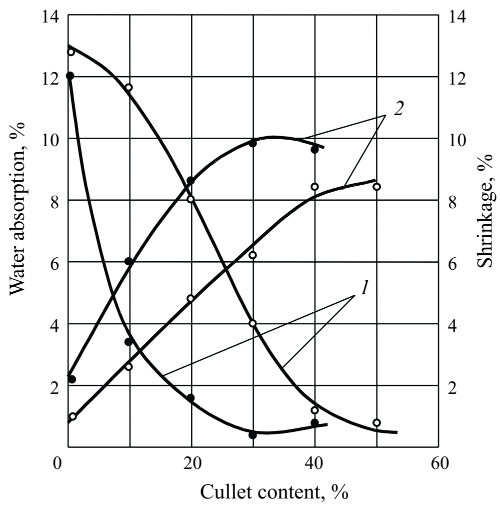

Fig. 1. The effect of cullet content on water absorption (*1*) and shrinkage (*2*) of Izykhskoe (○) and Beloyarskoe (●) clays at 1100°C.

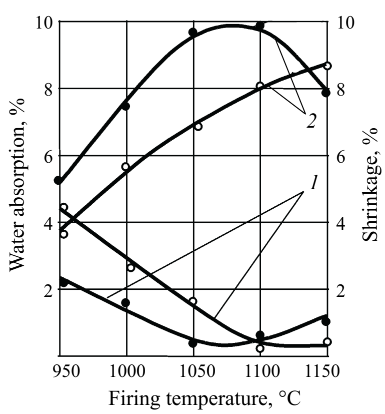

Fig. 2. The effect of firing temperature on water absorption (*1*) and shrinkage (*2*) of the binder. The cullet content is 50% and 30% in Izykhskoe (○) and Beloyarskoe clay(●), respectively.

binders based on Beloyarskoe clay with 30% cullet and Izykhskoe clay with 50% cullet fired at a temperature of 1100°C (Table 5).

TABLE 5

Mixture composition, %	Relative intensity of maximum phase reflections			
	quartz (4.22/2.27 Å)	nepheline (4.15 Å)	albite (4.01 Å)	anorthite (3.18 Å)
Clay (100)	4/2	–	–	3
Clay(70)* + cullet (30)	3/1	1	4	2
Clay(50) + cullet (50)	3/1	3	6	1
Sand(30) + binder (70) Clay(50) + cullet (50)	3/1	–	2	6
Sand(40) + clay (60)	3/1	–	–	4

* Beloyarskoe clay-based composition. Other compositions are based on Izykhskoe clay.

Moreover, x-ray phase analysis data indicate a possible interaction of the binder and the sand grains with their subsequent enrichment with the products of this interaction. This results from the enhancement of the relative intensity of the anorthite reflection on the x-ray pattern of the fired binder/sand mixture. Here anorthite formation occurs most actively due to interaction of sand with the low-melting binder (the relative intensities of anorthite reflections observed on x-ray patterns of samples of clay and clay/sand mixture are presented in Table 5).

It was assumed that the high sintering capacity of the binders, the affinity of the binders to the sand grains, and their reaction ability regarding the grain surface ensure sintering of granular compositions due to the binders thus used. The effect of the composition and quantity of the binder based on Izykhskoe clay on the sintering of granular compositions was studied for medium-grain sand (see Table 1, sample 2). Sintering of the blend was studied on the cylinder-samples (25-mm diameter and 25-mm height). The sand was mixed with a binder preliminarily wetted to 10%, and the samples were pressed at 25 MPa, dried at 105°C for 30 min, fired at 1100 – 1150°C, and kept over a 30-min period at the maximum temperature. The amount of binder in the mixture varied from 30 to 70% (the cullet content in the binder ranged within 30 – 50%).

The sand/binder sintering temperature exceeds the sintering temperature of the binder by 20 – 50°C. The lower the binder content in the mixture, the higher the temperature increment. Thus, Izykhskoe samples containing to 50% cullet sinter almost to zero water absorption at a temperature of 1100°C (see Fig. 1). The samples of the sand/binder mixture sinter at 1120°C or 1150°C, when the binder content in the mixture is 70% or 30%, respectively (Fig. 3).

A change in the grain composition of the sand did not affect the trend of increase in the sintering temperature of the binder-containing mixtures with the exception of fine-grained mixtures of the sand with 70% binders containing a substantial amount of the cullet (40 – 50% for Izykhskoe clay based binders, and 25 – 30% for Beloyarskoe clay based binders). The sintering temperature of these compositions decreases by 10 – 20°C against the temperature of binder sintering.

An increase in the sintering temperature (although more substantial, 100 – 150°C) or theexposure was also observed upon sintering multichamotte masses with a clayey binder [1]. Most probably, the increase in the sintering temperature was attributable to the same cause.

The sand grains, like chamotte grains, distort the structure homogeneity characteristic of the samples of the fine binder, thus inhibiting mixture sintering. However, since the sand grains (unlike chamotte grains) actively participate in melt formation [4] (the large-size grains from the surface and flour particles in full), this temperature increase is not large and even in the case of low binder content in the mixture the increase in the temperature is no more than 50°C. When the

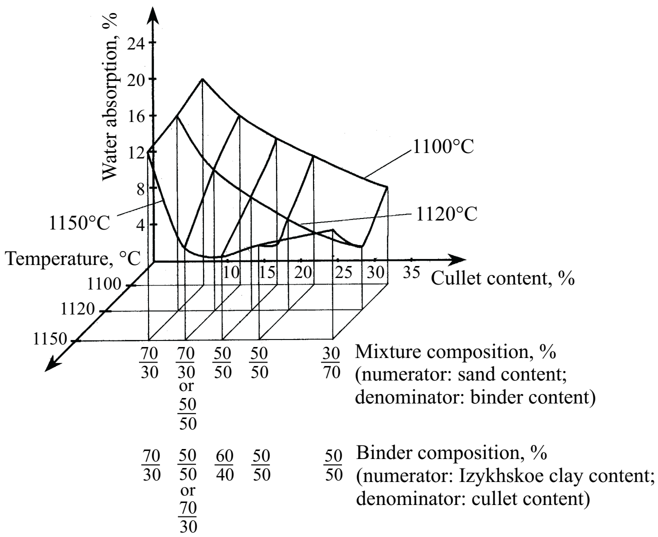

Fig. 3. The effect of the composition and amount of the binder and the firing temperature on the water absorption of medium-grained sand.

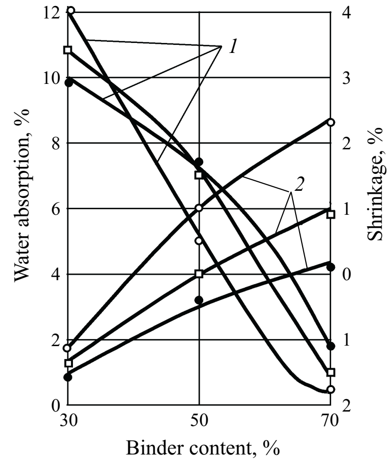

Fig. 4. The effect of binder content (Izykhskoe clay 60% and cullet 40%) on water absorption (*1*) and shrinkage (*2*) of the samples: coarse-grained sand (●), medium-grained sand (□), and fine-grained sand (○). Firing temperature is 1120°C.

binder content in the mixture is rather high, readily sintering seams bulge, the amount of one-shot melt increases upon firing, and the increase in the sintering temperature reduces to 20°C and, in the case of fine-grained sand, which contains a substantial amount of the flour fraction (thus increasing the fluxing capacity of the binder), totally disappears.

Coarse-sand-based mixtures sinter better when small amounts of the binder (30%) are used and the firing temperature ranges within 1100 – 1120°C.

Mixtures containing fine- and medium-grained sand (Fig. 4) sinter better as the amount of the binder or the firing temperature increases. Here the samples undergo expansion or shrinkage and change their color and surface state depending on the degree of sintering.

The expansion of samples having more than 10% water absorption is smaller (1.2%) when fine- or medium-grained sands are used in the mixture. For mixtures containing coarse sand the expansion is somewhat larger (1.6%). As the quality of the sintering increases, mixtures with fine- and medium-grained sands exhibit shrinkage up to 2.4% at zero water absorption, and mixtures containing coarse-grained sand only 0.4%.

The color and state of the sample surface depend on the degree of sintering and change as follows. Samples having a water absorption of 6% or more keep their initial pink color of the sand and look like a natural stone, granite. Most exciting are coarse-sand samples of uniform pink color and a concise granular surface. Samples having a water absorption less than 6% change color from pink to gray and vitrify (from the surface), thus gaining the structure of polished stone and keeping a porous base, which is extremely important to ensure good adhesive properties.

The changes in the sintering of the samples attributed to the grain composition of the sand in the mixture are determined (in our opinion) by the initial value of the intergrain hollowness and the simultaneous processes of liquid phase formation and polymorphic transformation of quartz, orthoclase, and anorthite.

Probably, the most dense initial grain packing upon using the coarse-grained sand and the significant increase in volume upon polymorphic transformation of the large grains result in a smaller water absorption (by 1.0 – 1.5%) and a larger expansion (by 0.4%) of samples prepared from coarse-sand-based mixtures containing a minimum amount of the binder and fired at 1100 – 1120°C. The amount of liquid phase thus formed does not facilitate marked migration of the grains. Hence, the water absorption of the samples is comparatively high (more than 6%) and the sample surface looks granular.

The increase in the amount of the liquid phase attributed to an increase in the binder content in the mixture or to an increase in the firing temperature facilitates migration of the sand grains, thus optimizing the grain arrangement and re-

TABLE 6

Component	Weight content, %					
	1	2	3	4	5	6
Sand:						
coarse-grained	70	50	–	–	–	70
medium-grained	–	–	50	50	–	–
fine-grained	–	–	–	–	70	–
Cullet content in the binder, %:						
50	30	50	–	–	30	30
40	–	–	–	50	–	–
30*	–	–	50	–	–	–

* Beloyarskoe clay-based composition. Other compositions are based on Izykhskoe clay.

TABLE 7

Index*	Tile composition					
	1	2	3	4	5	6
Firing temperature, °C	1120	1090	1090	1120	1150	1150
Water absorption, %	9.40	13.80	10.10	5.60	0.25	0.62
Shrinkage, %	+ 0.8	+ 0.3	+ 0.4	1.2	2.1	0.4
Strength, MPa:						
bend	210	197	220	230	260	270
compression	22	18	20	26	29	29
Moist expansion, %	0.12	0.11	0.10	0.09	0.08	0.10
Color	Pink		Brown	Gray	Gray**	

* Cold resistance of the tiles exceeded 50 cycles.

** Vitrified surface.

ducing the intergrain hollowness, which, in turn, results in shrinkage growth and reduction of the water absorption of the samples. Orthoclase decomposition (at temperatures above 1100°C) into leucite and glassy phase is accompanied by change in the sample color from pink to gray, whereas more intense sintering of the samples entails their vitrification.

Incorporation of flour (powdered) particles present in an amount of 8 – 16% in fine- and medium-grained sands during formation of the liquid phase promotes a decrease in the water absorption of the samples to zero values. High initial intergrain hollowness and reduced dilatation upon polymorphic transformation of fine and medium grains compared to coarse grains determine higher shrinkage of the samples (up to 2.4%).

Proceeding from the results obtained (see Figs. 3 and 4) we adopted compositions of the mixtures to be studied after firing. The sand content in the mixtures was 50 and 70%, and the amount of cullet in the binder ranged from 30 to 50% for the different types of clays (Table 6). Determination of the properties was performed on tiles measuring $125 \times 65 \times 10$ mm and on sample cylinders manufactured under laboratory conditions according to the aforementioned procedure.

Tiles for different purposes were obtained at different firing temperatures (Table 7): pane tiles (1120°C), facing tiles (1090°C), and floor tiles (1150°C). After firing, sightly tiles exhibit high bend (18 – 29 MPa) and compression strength (190 – 270 MPa), high cold resistance (more than 50 cycles), and small shrinkage (from + 0.8 to – 2.1%).

Thus, waste granular quartz-feldspar sands can be successfully used as a finished component in combination with ceramic binders in production of ceramic tiles for various purposes.

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